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① Applicant: **mitsui toatsu chemicals inc.**
No. 2-5, Kasumigaseki 3-chome
Chiyoda-Ku Tokyo 100(JP)

② Inventor: **INOMATA, Masamitsu**
2791-1, Mutsuno Mobara-shi
Chiba 297(JP)

Inventor: **SHIOTANI, Naokazu**
2100, Tougou Mobara-shi
Chiba 297(JP)

Inventor: **KOSHIZUKA, Kazuo**
2142, Tougou Mobara-shi
Chiba 297(JP)

Inventor: **KARASAWA, Minato**
226-1, Takashi Mobara-shi
Chiba 297(JP)

⑦ Representative: **Schüler, Horst, Dr.**
Kaiserstrasse 69
W-6000 Frankfurt/Main 1(DE)

⑤ **PROCESS FOR PRODUCING NORCAMPHANEDICARBONITRILES.**

⑦ A process directed to solving the problems of the conventional processes, such as low conversion, low selectivity, and high cost. The process comprises adding hydrogen cyanide to bicyclo[2.2.1]-5-heptene-2-carbonitrile in the presence of a nickel (0) complex catalyst and a Lewis acid.

EP 0 417 325 A1

PROCESS FOR PRODUCING NORCAMPHANE DICARBONITRILES

Technical Field

The present invention relates to a process for producing a norcamphane dicarbonitrile (hereinafter referred to as "NDC") compound, and more particularly, to a process for producing a norcamphane dicarbonitrile compound mainly composed of 2,5-norcamphane dicarbonitrile (hereinafter referred to as "2,5-NDC") and 2,6-norcamphane dicarbonitrile (hereinafter referred to as "2,6-NDC") comprising hydrocyanation of bicyclo [2,2,1]-5-heptene-2-carbonitrile (hereinafter referred to as "BHC").

Background Art

In the past only the following processes for producing NDC's by hydrocyanation of BHC were known :

- (i) A process where a catalyst system comprising a cobalt carbonyl catalyst and triphenyl phosphine is used (see U.S. Patent Nos. 2,666,780 and 2,666,748).
- (ii) A process where a catalyst system composed of tetrakis (triaryl phosphite) palladium and triphenyl phosphite is used (Am. Chem. Soc. Div. Pet. Chem. Preprints, 14 , B 29 (1969), etc.
- (iii) U.S. Patent No. 3,496,217 discloses a process for producing dinitriles such as adiponitrile and the like which comprises hydrocyanation of olefins such as 3-pentenitrile, 4-pentenitrile and the like in the presence of a zero-valent nickel complex and a promoter such as zinc chloride and the like.
- (iv) U.S. Patent Nos. 3,655,723 and 3,766, 237 disclose examples where a zero-valent nickel complex and zinc chloride are used upon hydrocyanation of methyl bicyclo (2,2,1)-5-heptene-2-carboxylate as a bicyclo (2,2,1)-5-heptene compound, and U.S. Patent No. 3,752,839 discloses examples using a zero-valent palladium catalyst and zinc chloride catalyst system.
- (v) Examples using a zero-valent nickel complex and zinc chloride are disclosed in U.S. patent Nos. 3,850,973 and 3,925,445 which are directed to a process for producing cyanoolefins by hydrocyanation of butadiene and bicyclo (2,2,1)-2,5-heptadiene, and in U.S. patent No. 4,215,068 which is directed to a process for producing a dicyanocyclopentane by hydrocyanation of cyclopentadiene and then hydrocyanation of the resulting product, cyanocyclopentene.

However, it can not be said that prior art has proposed a satisfactory process for producing NDC's.

For example, in (i) above, the yield of NDC's is only about 62 % when a cobalt catalyst and triphenyl phosphine are used in an amount of 15 - 30 % by weight based on BHC and hydrogen cyanide is used in a large amount, that is, 1.4 time that of BHC followed by carrying out the reaction at 130 ° C for 8 hours.

According to the production process of (ii) above, since an expensive palladium catalyst is used, recovery of the catalyst is troublesome, and the reaction temperature is so high (150 - 190 ° C) that handling is difficult, and further, as is clear from the low yield, the catalytic activity is low.

In the hydrocyanation of olefins and dienes in (iii) and (v), a zero-valent nickel complex is used in a large amount, i.e. about 0.5 - 2.5 mol % based on the olefin while the conversion of olefins and dienes is 30 - 80 % and the yield of the end product, dinitriles, is as low as 30 - 70 %. In addition, products and yields are not disclosed in the hydrocyanation of bicyclo (2,2,1)-5-heptene compounds in (iv) above.

An object of the present invention is to solve the above-mentioned problems of the prior art and produce NDC's at a high conversion, high selectivity and advantageously from an economical point of view.

Disclosure of Invention

The present invention is a process for producing a norcamphane dicarbonitrile (NDC) comprising hydrocyanation of bicyclo [2,2,1]-5-heptene-2-carbonitrile (BHC) in the presence of a zero-valent nickel complex catalyst and a Lewis acid.

BHC used in the present invention may be easily obtained in a high yield by the Diels-Alder reaction of cyclopentadiene with acrylonitrile by heating, and it is preferable to use a product obtained by purifying the reaction product by distillation or the like.

The zero-valent nickel complex catalyst used in the present invention can be represented by the general formula (I),



where A,B,C and D are, similar or dissimilar, and are neutral ligands represented by the general formula (II),

P (x)(y)(z) (II)

where p is a phosphorus, x, y and z are, similar or dissimilar, OR where R is selected from the group consisting of alkyl having 18 carbon atoms or less and aryl having 18 carbon atoms or less.

Examples of the neutral ligands include triaryl phosphites such as triphenyl phosphite and the like; tri-substituted phenyl phosphite such as tri-halo substituted phenyl phosphite, tri-alkoxy substituted phenyl phosphite, tri-alkyl substituted phenyl phosphite; and trialkyl phosphites, and mixtures thereof.

Concrete examples of tri-substituted phenyl phosphites include tri-m- or p-tolyl phosphite, tri-m or p-chlorophenyl phosphite, tri-m or p-methoxyphenyl phosphite, and tri-m or p-nonylphenyl phosphite. Concrete examples of trialkyl phosphites include triethyl phosphite, triisopropyl phosphite, and tributyl phosphite.

One or more of the neutral ligands, A, B, C and D can leave the zero-valent nickel complex catalyst under most reaction conditions.

The neutral ligands are preferably triaryl phosphites, in particular, triphenyl phosphite, tri-m or p-tolyl phosphite, and tri-m or p-nonylphenyl phosphite.

Exemplary suitable zero-valent nickel complex catalysts include tetrakis (triphenyl phosphite) nickel; tetrakis (tri-substituted phenyl phosphite) nickels, for example, tetrakis (tri-halo-substituted phenyl phosphite) nickel, tetrakis (tri-alkoxy-substituted phenyl phosphite) nickel and tetrakis (tri-alkyl-substituted phenyl phosphite) nickel; and tetrakis (trialkyl phosphite) nickel.

As concrete examples of tetrakis (tri-substituted phenyl phosphite) nickels are those where the tri-substituted phenyl phosphite is selected from tri-m- or p-tolyl phosphite, tri-m- or p-chlorophenyl phosphite, tri-m- or p-methoxyphenyl phosphite, tri-m- or p-nonylphenyl phosphite and the like.

Further, exemplary suitable zero-valent nickel complex catalysts include tetrakis (trialkyl phosphite) nickel, for example, tetrakis (triethyl phosphite) nickel, tetrakis (triisopropyl phosphite) nickel, and tetrakis (tributyl phosphite) nickel.

In the present invention, it is preferable to carry out hydrocyanation in the presence of a neutral ligand so as to enhance the activity of the zero-valent nickel complex catalyst and prolong the life of the catalyst.

The amount of the neutral ligand used is usually one mole or more, preferably 2 - 32 moles, more preferably 4 - 16 moles based on one mole of the existing zero-valent nickel complex catalyst. An amount exceeding 32 moles does not adversely affect the reaction itself, but is not always economically preferable taking into consideration the post-treatment of the reaction product fluid and the loss of the neutral ligand upon the purification and recovery procedure.

Taking into account the neutral ligand coordinate in the zero-valent nickel complex, the amount of the total neutral ligand used is usually 5 moles or more, preferably 6 - 36 moles, more preferably 8 - 20 moles per mole of the zero-valent nickel complex catalyst.

Preparation of the zero-valent nickel complex catalyst is disclosed, for example, in U.S. Patent No. 3,328,443, J. Chem. Soc. London, 1378 - 1389 (1960), J. Am. Chem. Soc., 81, 4200 - 4209 (1959) and Inorg. Synth., 13, 108 or 112.

The amount of the zero-valent nickel complex catalyst used in terms of the molar ratio of zero-valent nickel complex catalyst to BHC is usually from 1 : 5000 to 1 : 20, preferably from 1 : 2000 to 1 : 100. When the molar ratio exceeds 1 : 20, there is not obtained an advantage corresponding to the increase in the amount of the catalyst and thereby it is not economical.

In the present invention, a Lewis acid is present as a promoter. As a Lewis acid, there is, for example, a compound comprising a center metal having a vacant orbit.

Examples of Lewis acids are compounds composed of an anion and a metallic cation selected from elements of groups IIa, IIIa, IVa, Va, VIa, VIIa, VIII, Ib, IIb, IIIb, and IVb of the Periodic Table.

Examples of the metallic cation are zinc, cadmium, beryllium, aluminum, gallium, indium, silver, titanium, zirconium, hafnium, germanium, tin, vanadium, niobium, scandium, chromium, molybdenum, tungsten, manganese, rhenium, palladium, thorium, erbium, iron, cobalt, and boron ions.

Examples of anions are halogen anions such as chlorine, bromine, fluorine and iodine, anions of lower fatty acids of C₂-C₇, HPO₃²⁻, H₂PO₂⁻, CF₃CO₂⁻, OSO₂C₇F₁₅⁻, and SO₄²⁻.

Particularly preferable metallic cations are zinc, cadmium, titanium, tin, vanadium, chromium, aluminum and the like ions and examples of anions are chlorine ion, iodine ion, HPO₃²⁻, H₂PO₂⁻ and the like.

In addition, examples of a Lewis acid are organic boron, for example, trialkyl boron such as triethyl boron, triphenyl boron and the like, and metal alkoxides such as aluminum isopropoxide and titanium isopropoxide.

Examples of preferable Lewis acids are zinc chloride, cadmium chloride, cadmium iodide, chromium chloride, boron trichloride, and triphenyl boron, and zinc chloride is particularly preferable.

A Lewis acid as a promoter can prolong the life of the catalyst and the amount of Lewis acid used is

usually 0.05 - 50 moles, preferably 0.5 - 5 moles per mole of the zero-valent nickel complex catalyst.

In the hydrocyanation of the present invention, the neutral ligand can behave as a solvent, but additionally other solvent or solvents may be used.

The solvents used include, for example, aryl compounds containing at least one hydroxyl group and
 5 having 6 - 20 carbon atoms, preferably, 6 - 10 carbon atoms, and if desired, may be the above-mentioned aryl compounds having at least one substituent selected from the group consisting of fluoro, chloro, bromo, iodo, nitro, cyano, and hydrocarbon groups having 1 - 9 carbon atoms. The aryl compounds are, for example, phenol, p-cresol, resorcinol, β -naphthol, p-chlorophenol, p-nitrophenol, p-butylphenol and analogs thereof.

10 As other solvents, there may be mentioned, for example, aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene and the like; nitriles such as acetonitrile, benzonitrile and the like; ethers such as dioxane, o-dimethoxybenzene, tetrahydrofuran, dimethoxyethane, diethoxyethane and the like; chloroaromatic hydrocarbons such as o-dichlorobenzene, p-dichlorobenzene and the like; and analogs thereof.

15 According to the present invention, the hydrocyanation of BHC can be effected, for example, such that prescribed amounts of the above-mentioned zero-valent nickel complex catalyst, Lewis acid, BHC, and neutral ligand (or solvent) are fed to a reactor and then hydrogen cyanide is introduced into the reaction fluid under stirring at a prescribed temperature. Hydrogen cyanide may be introduced therein in the form of either gaseous hydrogen cyanide or liquid hydrogen cyanide.

20 Hydrogen cyanide may be used alone, but, from the standpoint of handling, it is desirable to dilute hydrogen cyanide to an appropriate concentration with a gas inert to the reaction such as nitrogen, helium, argon and the like.

Liquid hydrogen cyanide may be used alone or may be diluted with a solvent such as benzene, xylene and the like to an appropriate concentration for use.

25 Hydrogen cyanide is used usually in an amount of 0.2 - 1.5 mole, preferably 0.5 - 1.2 mole per mole of BHC.

The reaction temperature of hydrocyanation of BHC is usually in the range of from -20 to 200°C , preferably from 20 to 130°C , more preferably from 50 to 100°C .

30 The reaction pressure is, in usual, preferably atmospheric pressure, and the reaction may be effected at a pressurized system, but there is not any remarkable advantage due to the high pressure.

The hydrocyanation of BHC is usually effected batchwise, but a continuous reaction system may be employed such that BHC, hydrogen cyanide, zero-valent nickel complex catalyst, Lewis acid, neutral ligand and the like are continuously fed to a reactor.

35 NDC's produced by the present invention can be obtained as a mixture containing 2,5-NDC and 2,6-NDC as the components.

After completion of the reaction, the resulting reaction product fluid containing NDC's produced by hydrocyanation of BHC at a high concentration is subjected to a post-treatment, for example, for recovering effective components as catalyst and the like, that is, extraction with an organic solvent or extracting Lewis acids and inorganic materials with water, and then NDC's are obtained by distillation.

40 Distillation of NDC's is preferably carried out at a pressure of 0.3 - 0.5 mm Hg to collect a distillate fraction at 120 - 130°C as NDC's.

45 According to the present invention, NDC's can be produced at high conversion and at high selectivity economically by hydrocyanation of BHC in the presence of a zero-valent nickel complex catalyst and a promoter system composed of a Lewis acid, and therefore, the process for producing NDC's is very advantageous.

Best Mode for Carrying Out the Invention

50 For the purpose of describing the present invention more in detail, the following examples are given. Comparative examples are also given to help the understanding of the present invention.

Analysis of the reaction fluid was conducted by gas chromatography.

55 EXAMPLE 1

A 50 ml. glass round-bottom flask fitted with a stirrer, a thermometer, a gas inlet tube, a cooler and the like was charged with BHC 27.55 g (229 mmol), tetrakis (triphenyl phosphite) nickel 0.79 g (0.608 mmol),

zinc chloride 0.44 g (3.2 m mol) and triphenyl phosphite 3.10 g (10.0 m mol), purged with a nitrogen gas sufficiently, and the contents in the reactor was kept at 95 °C with stirring.

Then, nitrogen gas was introduced into a receiving vessel containing liquid hydrogen cyanide cooled with ice water and bubbled through the liquid hydrogen cyanide to generate a hydrogen cyanide gas and said gas was introduced into the reaction fluid in the reactor.

The flow rate of nitrogen gas was 55 - 60 ml/min. 7.0 g (259 m mol) of hydrogen cyanide gas in total was fed to the reactor over 5 hours and then the reaction was completed.

The reaction fluid was cooled and analyzed, and it was found that the conversion of BHC was 97.5 % and selectivity of NDC's 94.4 %.

EXAMPLES 2 - 6

The procedure of Example 1 was repeated using the same reactor as in Example 1 except that molar ratio of BHC, tetrakis (triphenyl phosphite) nickel, zinc chloride, triphenyl phosphite and hydrogen cyanide, temperature and feeding time of hydrogen cyanide gas were changed.

The results are shown in Table 1.

EXAMPLE 7

The reaction of Example 1 was repeated except that liquid hydrogen cyanide cooled with ice was directly fed to the reactor using a microtube pump in place of the hydrogen cyanide gas.

The flow rate of liquid hydrogen cyanide was 2 - 2.5 ml/hr, and 7.0 g (259 m mol) of liquid hydrogen cyanide in total was fed to the reactor over 5 hours and the reaction was completed.

The reaction fluid was cooled and analyzed. It was found that the conversion of BHC was 99.9 % and selectivity of NDC's 99.8 % (see Table 2).

EXAMPLES 8 - 9

The procedure of Example 7 was repeated except that the molar ratio of liquid hydrogen cyanide, temperature, and feeding time of hydrogen cyanide were changed.

The results are shown in Table 2.

EXAMPLES 10 - 13

The procedure of Example 6 was repeated with the same feed as in Example 6 except that the zero-valent nickel complex catalyst and the neutral ligand were replaced with the catalyst systems shown in Table 3. The results are shown in Table 3.

EXAMPLES 14 - 18

The hydrocyanation of Example 6 was repeated with the same feed as in Example 6 except that Lewis acids in Table 4 were used in place of zinc chloride. The results are shown in Table 4.

Table 1

	Molar ratio				Gaseous H C N	Tempera- ture (°C)	H C N Feeding Time (hr)	B H C Conversion (%)	N D C 's Selectivity (%)
	BHC	Ni (O)	ZnCl ₂	P (OPh) ₃					
Example 1	100	0.27	1.41	4.16	113	95	5	97.5	94.4
Example 2	100	0.13	0.64	1.25	130	95	4.8	100.0	95.5
Example 3	100	0.066	0.32	0.50	136	95	2.8	80.7	99.0
Example 4	100	0.13	0.65	1.00	99	81	4.5	91.3	97.0
Example 5	100	1.00	1.00	1.50	120	130	2.5	100.0	99.8
Example 6	100	0.14	0.16	1.01	131	50	4.5	99.9	99.4

Ni (O) : Tetrakis (triphenyl phosphite) nickel

P (OPh)₃ : Triphenyl phosphite

Table 2

	Molar ratio				Tempera- ture (°C)	H C N Feeding Time (hr)	B H C Conversion (%)	N D C's Selectivity (%)
	BHC	NI (O)	ZnCl ₂	P (OPh) ₃				
Example 7	100	0.27	1.41	4.16	113	5	99.9	99.8
Example 8	100	0.27	1.41	4.16	140	3	100	99.3
Example 9	100	0.27	1.41	4.16	95	5	94.9	98.9

Table 3

	Ni (O)	Neutral ligand	B H C Conversion (%)	N D C's Selectivity (%)
Example 10	$\text{Ni} \left[\text{P} \left(\text{O}-\text{C}_6\text{H}_4-\text{CH}_3 \right)_3 \right]_4$	$\text{P} \left(\text{O}-\text{C}_6\text{H}_4-\text{CH}_3 \right)_3$	100	99.5
Example 11	$\text{Ni} \left[\text{P} \left(\text{O}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{CH}_3 \right)_3 \right]_4$	$\text{P} \left(\text{O}-\text{C}_6\text{H}_3(\text{CH}_3)-\text{CH}_3 \right)_3$	100	99.4
Example 12	$\text{Ni} \left[\text{P} \left(\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3 \right)_3 \right]_4$	$\text{P} \left(\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3 \right)_3$	100	99.6
Example 13	$\text{Ni} \left[\text{P} \left(\text{O}-\text{C}_6\text{H}_4-\text{Cl} \right)_3 \right]_4$	$\text{P} \left(\text{O}-\text{C}_6\text{H}_4-\text{Cl} \right)_3$	100	99.5

Table 4

	Lewis acid	B H C Conversion (%)	N D C's Selectivity (%)
5			
10	Example 14 SnCl_2	97.2	99.3
	Example 15 CdCl_2	98.5	99.7
15	Example 16 CrCl_3	95.6	99.5
	Example 17 Al (O-iPr)_3	85.9	99.0
20	Example 18 BPh_3	99.9	99.8

25 Al (O-iPr)_3 : Aluminum isopropoxide

BPh_3 : Triphenyl boron

30 COMPARATIVE EXAMPLE 1

The reaction of Example 1 was repeated with the same feed as in Example 1 except that tetrakis (triphenyl phosphite) nickel was replaced with 0.82 g (0.608 m mol) of tetrakis (triphenyl phosphite) palladium. As a result, the conversion of BHC was 31.6 % and the selectivity of NDC's 93.1 %.

35 COMPARATIVE EXAMPLE 2

40 The reaction of Example 6 was repeated with the same feed as in Example 6 except that zinc chloride was not used.

As a result, the conversion of BHC was 4.1 % and the selectivity of NDC's 21.5 %.

45 Industrial Applicability

NDC's produced by the present invention can be hydrogenated to prepare the corresponding diamines, and the diamines may be reacted with aliphatic dicarboxylic acids to produce polyamide resins. Therefore, the NDC's are useful as intermediates for organic syntheses.

50 Claims

55 1. A process for producing a norcamphane dicarbonitrile which comprises hydrocyanation of bicyclo [2,2,1]-5-heptene-2-carbonitrile in the presence of a zero-valent nickel complex catalyst and a Lewis acid.

2. A process according to claim 1 wherein hydrocyanation is effected in the presence of a neutral ligand.

3. A process according to claim 1 or claim 2 wherein the zero-valent nickel complex catalyst is represented by the general formula (I),

$$\text{Ni} [\text{(A)} \text{(B)} \text{(C)} \text{(D)}] \text{(I)}$$
 where A, B, C and D are, similar or dissimilar, neutral ligands of formula (II),

$$\text{P} \text{(x)} \text{(y)} \text{(z)} \text{(II)}$$
 where P is a phosphorus atom, x, y and z are similar or dissimilar groups represented by OR where R is selected from the group consisting of alkyl having 18 carbon atoms or less and aryl having 18 carbon atoms or less.
4. A process according to claim 2 wherein the neutral ligand is a compound of the general formula (II),

$$\text{P} \text{(x)} \text{(y)} \text{(z)} \text{(II)}$$
 where P is a phosphorus atom and x, y and z are similar or dissimilar groups represented by OR where R is selected from the group consisting of alkyl having 18 carbon atoms or less and aryl having 18 carbon atoms or less.
5. A process according to claim 3 wherein the zero-valent nickel complex catalyst is tetrakis (triaryl phosphite) nickel or tetrakis (trialkyl phosphite) nickel.
6. A process according to claim 5 wherein the zero-valent nickel complex catalyst is tetrakis (triphenyl phosphite) nickel or tetrakis (tri-substituted phenyl phosphite) nickel.
7. A process according to claim 6 wherein the tetrakis (tri-substituted phenyl phosphite) nickel is a member selected from the group consisting of tetrakis (tri-halo-substituted phenyl phosphite) nickel, tetrakis (tri-alkoxy-substituted phenyl phosphite) nickel and tetrakis (tri-alkyl-substituted phenyl phosphite) nickel.
8. A process according to claim 7 wherein the tetrakis (tri-substituted phenyl phosphite) nickel is a member selected from the group consisting of tetrakis (tri-m or p-tolyl phosphite) nickel, tetrakis (tri-m or p-chlorophenyl phosphite) nickel, tetrakis (tri-m or p-methoxyphenyl phosphite) nickel and tetrakis (tri-m or p-nonylphenyl phosphite) nickel.
9. A process according to claim 5 wherein the tetrakis (trialkyl phosphite) nickel is a member selected from the group consisting of tetrakis (triethyl phosphite) nickel, tetrakis (triisopropyl phosphite) nickel and tetrakis (tributyl phosphite) nickel.
10. A process according to claim 1 or claim 2, wherein the Lewis acid is a compound composed of an anion and a metal cation of an element selected from the group consisting of groups IIa, IIIa, IVa, Va, VIa, VIIa, VIII, Ib, IIb, IIIb, and IVb of the Periodic Table.
11. A process according to claim 10 wherein the Lewis acid contains a cation of a metal selected from the group consisting of zinc, cadmium, beryllium, aluminum, gallium, indium, silver, titanium, zirconium, hafnium, germanium, tin, vanadium, niobium, scandium, chromium, molybdenum, tungsten, manganese, rhenium, palladium, thorium, erbium, iron, cobalt, and boron.
12. A process according to claim 10 wherein the anion of the Lewis acid is an anion selected from the group consisting of halogen anions, that is, chlorine bromine, fluorine and iodine, anions of lower fatty acid of C₂-C₇, HPO₃²⁻, H₂PO₂⁻, CF₃CO₂⁻, OSO₂C₇F₁₅⁻, and SO₄²⁻.
13. A process according to claim 11 wherein the anion of the Lewis acid is an anion selected from the group consisting of halogen anions, that is, chlorine, bromine, fluorine and iodine, anions of lower fatty acid of C₂-C₇, HPO₃²⁻, H₂PO₂⁻, CF₃CO₂⁻, OSO₂C₇F₁₅⁻, and SO₄²⁻.
14. A process according to claim 11 wherein the metal cation of the Lewis acid is a metal cation selected from the group consisting of zinc, cadmium, titanium, tin, vanadium, chromium, and aluminum ions.
15. A process according to claim 12 wherein the anion of the Lewis acid is a member selected from the group consisting of chlorine ion, iodine ion, HPO₃²⁻ and H₂PO₂⁻.

16. A process according to claim 1 or claim 2 wherein the Lewis acid is a member selected from the group consisting of zinc chloride, cadmium chloride, cadmium iodide, chromium chloride, boron trichloride and triphenyl boron.
- 5 17. A process according to claim 16 wherein the Lewis acid is zinc chloride.
18. A process according to claim 1 or claim 2 wherein the Lewis acid is organic boron or metal alkoxide.
- 10 19. A process according to claim 18 wherein the Lewis acid is a member selected from the group consisting of trialkyl boron, triphenyl boron, aluminum alkoxide and titanium alkoxide.
20. A process according to claim 1 or claim 2 wherein the molar ratio of the zero-valent nickel complex catalyst to bicyclo [2,2,1]-5-heptene-2-carbonitrile ranges from 1 : 5000 to 1 : 20.
- 15 21. A process according to claim 1 or claim 2 wherein the molar ratio of the zero-valent nickel complex catalyst to bicyclo [2,2,1]-5-heptene-2-carbonitrile ranges from 1 : 2000 to 1 : 100.
22. A process according to claim 1 or claim 2 wherein the molar ratio of the Lewis acid to the zero-valent nickel complex catalyst ranges from 0.05 : 1 to 50 : 1.
- 20 23. A process according to claim 1 or claim 2 wherein the molar ratio of the Lewis acid to the zero-valent nickel complex catalyst ranges from 0.5 : 1 to 5 : 1.
24. A process according to claim 2 wherein the total neutral ligand per mole of the zero-valent nickel complex catalyst is 5 moles or more.
- 25 25. A process according to claim 2 wherein the total neutral ligand per mole of the zero-valent nickel complex catalyst is 6 - 36 moles.
- 30 26. A process according to claim 2 wherein the total neutral ligand per mole of the zero-valent nickel complex catalyst is 8 - 20 moles.
27. A process according to claim 1 or claim 2 wherein the reaction temperature of hydrocyanation is in the range of from -20 to 200 ° C.
- 35 28. A process according to claim 1 or claim 2 wherein the reaction temperature is 20 - 130 ° C
29. A process according to claim 1 or claim 2 wherein the reaction temperature is 50 - 100 ° C.
- 40 30. A process according to claim 1 or claim 2 wherein hydrogen cyanide is introduced in the form of gas or liquid.
31. A process according to claim 1 or claim 2 wherein the molar ratio of hydrogen cyanide to BHC is in the range of from 0.2 : 1 to 1.5 : 1.
- 45 32. A process according to claim 1 or claim 2 wherein the molar ratio of hydrogen cyanide to BHC is in the range of from 0.5 : 1 to 1.2 : 1.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/00450

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵ C07C255/47, 253/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	C07C255/47, 253/00 - 253/12	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	JP, A, 57-156454 (E. I. du Pont de Nemours and Company), 27 September 1982 (27. 09. 82), Columns 1 to 3 & US, A, 4330483 & GB, A, 2093454 & BE, A, 892234 & DE, A, 3206643 & NL, A, 8200692 & FR, A, 2500445 & CA, A, 1175066	1 - 32
Y	US, A, 3655723 (E. I. du Pont de Nemours and Company), 11 April 1972 (11. 04. 72), Columns 13 and 14	1 - 32
Y	US, A, 3766237 (E. I. du Pont de Nemours and Company), 16 October 1973 (16. 10. 73), Columns 35 and 36	1 - 32
A	JP, A, 57-193438 (Hoechst AG), 27 November 1982 (27. 11. 82), Column 1 & EP, A, 65294 & DE, A, 3119819	1
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
June 8, 1990 (08. 06. 90)	June 25, 1990 (25. 06. 90)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		